Title: Thermal characterization of commercial HDPE and UHMWPE

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Abstract

Polyethylene (PE) is one of the most widely produced polymers in the world with applications in nearly every industry. To determine the applicability of PE for future projects at Los Alamos National Laboratory high density polyethylene (HDPE) and ultra-high molecular weight polyethylene (UHMWPE) grades were characterized by differential scanning calorimetry (DSC), and thermomechanical analysis (TMA) to understand the melting temperature, heat capacity, and coefficient of thermal expansion (CTE).

Introduction

Polyethylene is one of the world's most common polymers, with over 80 million tonnes produced every year. PE is produced from the monomer ethylene, derived from petrochemical sources, and has the chemical formula $(–C_2H_4–)_n$. PE is widely used for industrial, engineering, and commercial products due to its versatile mechanical, chemical, and thermal properties. PE has low strength, hardness, and rigidity, but is highly ductile. PE also has little creep resistance, the ability to resist deformation under a given load over time, at temperatures near its melt temperature. However, this can be improved by crosslinking the material or with additives. PE has high chemical resistance, is not hygroscopic, and has low permeability. Thermally PE has a melting point, depending upon the grade, anywhere in the range of 80-180°C. However, this does allow for ease of processing for various applications.[1,2]

The unique and versatile properties of PE are related to its chemical backbone and the degree of crystallinity and molecular weight. Because PE is comprised of long chains that may tightly pack together, the chains will interact forming crystalline regions in the polymer. Crystallinity and density of PE is affected by the branching and molecular weight, which is in turn controlled by the processing method. These differing methods give rise to different forms of PE including low density polyethylene (LDPE), HDPE, and UHMWPE.[1,3,4]

HDPE has a density between 0.94-0.96 g cm^{-3}. HDPE has less branching than LDPE resulting in higher crystallinity (70-90%). HDPE is produced under low pressures and the branching is controlled during polymerization by use of catalysts, including Ziegler-Natta catalysts. The decrease in branching results in greater intermolecular forces and slight increases in strength and thermal resistance. HDPE is used in diverse products such as, water bottles, pipes (storm drains), cable insulation, toys, and food packaging and storage.[1-3,5]

UHMWPE is a variation of PE with molecular weights in the millions. UHMWPE is semi-crystalline, typically with crystallinity less than that of HDPE. UHMWPE is extremely abrasion resistant finding applications for joint replacement. It can also spun into fibers and utilized in applications similar to that of Kevlar.[6-8]

PE is a valuable material due to its low melting point enabling ease of processing and its chemical resistance has led varied applications. Therefore, it is important to understand the thermal and mechanical characteristics of PE to determine its applicability for a particular use. DSC, modulated DSC (MDSC), and TMA were employed to determine the glass transition (T_g), melting point, heat of fusion, crystallinity, heat capacity, and CTE.

Experimental

Materials

Sheets of HDPE and UHMWPE were received from their respective manufacturers; Table 1 summarizes the six commercial PE products tested, their grades, and the supplier. Samples were tested as received.

Table 1: Commercial polymers tested with grade and the supplier listed.

Sample Name	PE Grade	Manufacturer
Densetec	HDPE	Polymer Industries
Hitec	HDPE	Vycom
Polystone G	HDPE	Rochling
Polyslick	UHMWPE	Polymer Industries
Tivar	UHMWPE	Quadrant
Polystone M	UHMWPE	Rochling

DSC

All experiments were performed on a TA instruments DSC Q2000 with a refrigerated cooling system 90, under 50 mL/min nitrogen purge with an empty T-zero aluminum hermetic pan as a reference. All samples were approximately 10 mg. The DSC was calibrated using indium verification. All samples were heated from -50°C to 200°C at 10/min.[9-11]

MDSC was utilized and calibrated using a sapphire standard between runs. Experiments were performed from -80°C to 100°C with a ramp rate of 3/min and a modulation of +/- 0.95 every 120s.[9-12]

TMA

All experiments were performed on a TA Instruments Q400 EM over a range of -55°C to 65°C with a ramp rate 2/min and a preload force of 0.1N. A nitrogen purge flowed at a rate of 50.00 mL/min. The instrument was calibrated using aluminum and indium standards. Each sample was machined to dimensions of 5mm x 5mm x 5mm. Three species of each sample were tested to obtain a standard deviation.[10,11]

<u>**Results and Discussion**</u>

DSC

The DSC data reveals the peak melt temperature, heat of fusion, and the as received crystallinity of the PE. Heat of fusion is measured by integrating over the range 60°C to 180°C, 5 crystallinity is the calculated heat of fusion divided by the heat of fusion of a 100% crystalline PE sample, 289 J/g. Table 2 summarizes this data for the samples. This reveals that the melt temperature is similar regardless of PE grade. Heat of fusion, however, is higher for HDPE grades; this is due to the higher crystallinity of HDPE compared to that of UHMWPE. This is confirmed in the calculated crystallinity, HDPE being much higher with over 75% crystallinity in all HDPE grades and 50-60% for the UHMWPE grades.

Table 2: Melt temperatures, heat of fusion, and as-received crystallinity of PE grades.

Sample	Peak Melt Temperature (°C)	Heat of Fusion (J/g)	% Crystallinity
Densetec	136.91	219.00	75.78
Hitec	139.20	240.90	83.36
Polystone G	137.39	225.30	77.96
Polyslick	136.13	152.80	52.87
Tivar	136.25	153.30	53.04
Polystone M	135.08	172.60	59.72

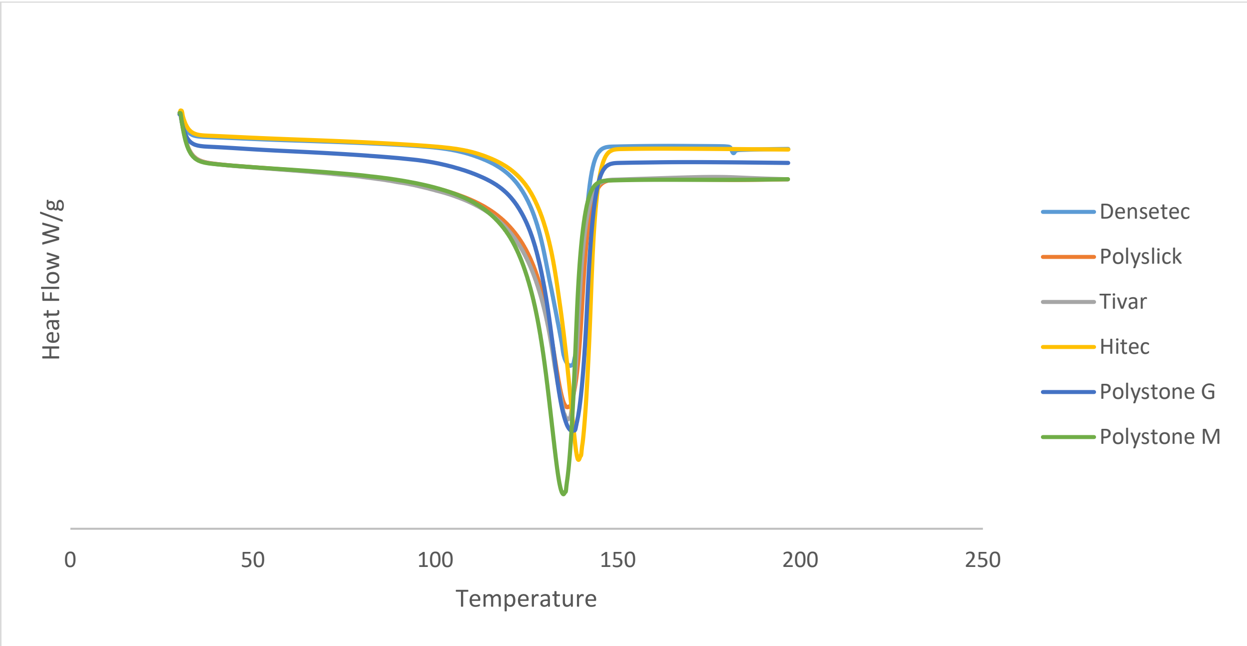

Figure 1: DSC data showing the PE grades and their melt peaks.

MDSC

MDSC is able to directly measure the heat capacity of a material. Heat capacity is the amount of heat required to raise the temperature of a material by a given amount. Heat capacity is directly related to the molecular mobility in polymers. This value is the capacity of the polymer to absorb heat through vibrations, rotations, and translations.[10] These samples being semi-crystalline have lower heat capacity than fully amorphous PE and greater than crystalline PE. UHMWPE do show slightly higher heat capacities due to those materials having regions that are more amorphous. There is also an increase around 60°C that has been attributed to the onset of melting.[10]

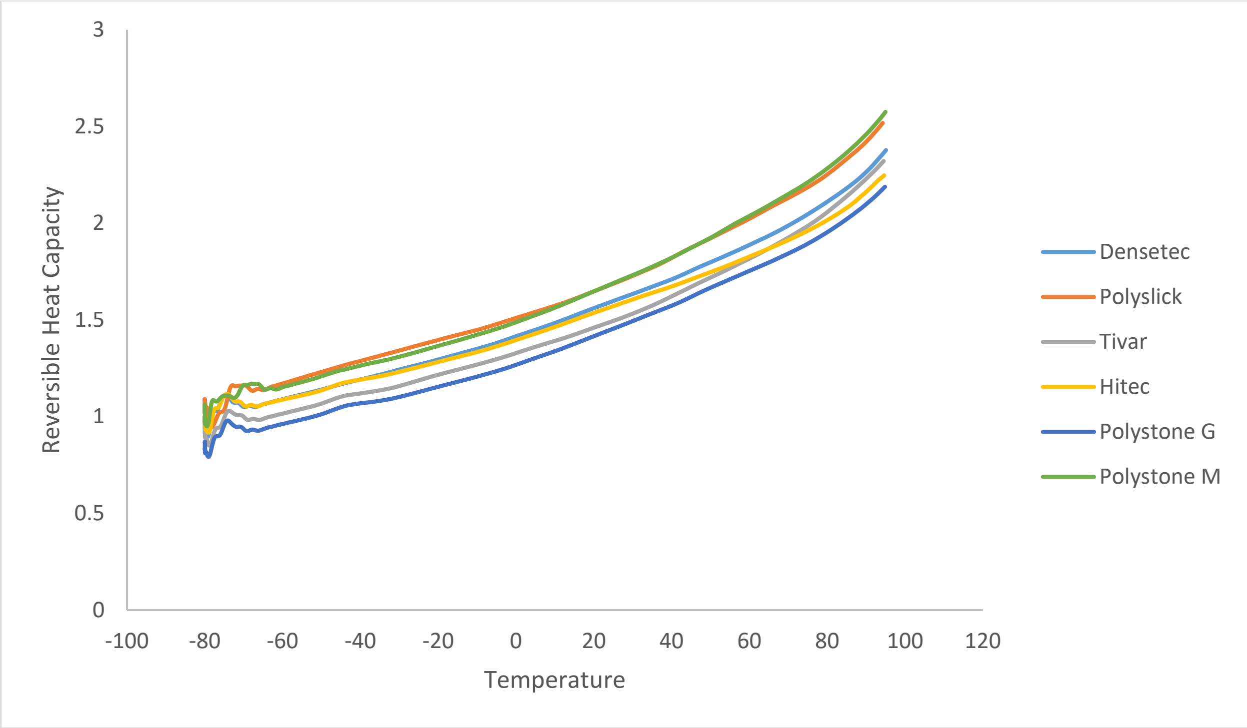

Figure 2: MDSC showing the reversible heat capacity of the PE grades.

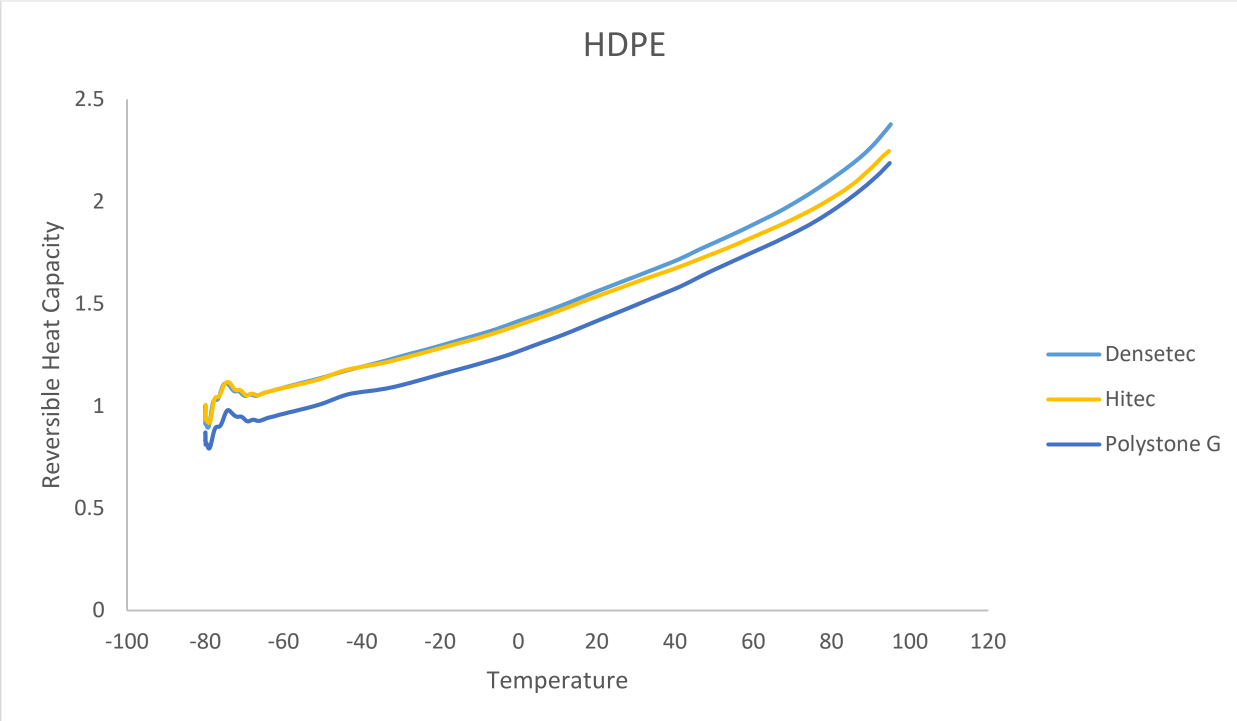

Figure 3: Heat capacity of HDPE grades.

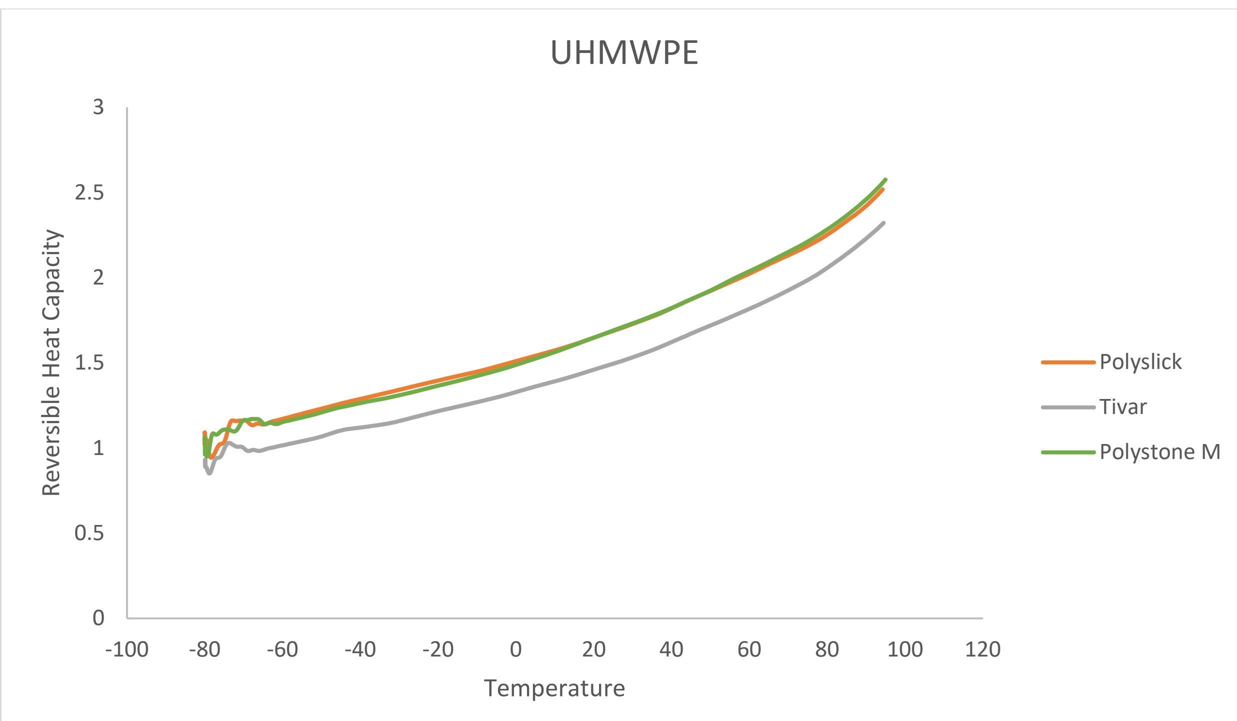

Figure 4: Heat capacity of UHMWPE grades.

TMA

TMA reveals the linear CTE, which is the slope of the line dL/L_0 vs. temperature. Where dL is the instantaneous change in length as a function of temperature and L_0 is the initial sample length. The slope changes slightly as the sample is heated, therefore, the temperature range is divided into three ranges to calculate the CTE. Table 3 summarizes the results for each sample in each temperature range. The general trend is UHMWPE expands more with temperature and this is related to the crystallinity of the sample.

Table 3: TMA data presenting CTE over given temperature range.

Sample	-55°C to -30°C	-30°C to 15°C	15°C to 65°C
Densetec	96	105	71
Polystone G	90	109	147
Polyslick	123	123	160
Tivar	118	131	124
Polystone M	115	125	151

Conclusion

Through thermal characterization, it was shown that HDPE has greater crystallinity than UHMWPE grades. This a higher percentage of crystallinity leads to higher melting temperatures, a decrease in heat capacity, and less thermal expansion. It has been reported that there is a transition for PE grades at -35°C, however, there was no transition observed in these samples.[10] An instrument that can reach lower temperatures must be employed to find this transition and other transitions reported. It may also be of value to employ other techniques such as dynamic mechanical analysis to characterize the materials.

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